Photoelectrochemical Hydrogen Production Using New Combinatorial Chemistry Derived Materials

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Objectives

- Continue synthesis and screening of libraries designed in year 1 and follow promising (lead) materials as they are identified.
- Explore the composition-function relationship of dopants in ZnO hosts.
- Investigate metal oxide libraries for electrocatalytic hydrogen production and expand our high-throughput screening to include relative electrocatalytic overpotential as a routine screen.
- Develop a high-throughput optical screening system to measure the effective bandgap of metal oxides in libraries.
- Synthesize and screen model libraries optically for bandgap as a primary screen; create secondary libraries of compositions with solar spectrum adsorption and subsequently screen the derivate libraries for appropriate redox/flatband levels and finally for H_2 production.
- Investigate library design for synthesis of semiconductor heterostructures utilizing two-photon absorption processes.
- Continue to expand our investigation of nanoporous materials with emphasis on the ZnO, WO_3 and TiO_2.
- Participate as a member of the USA Annex-14 Expert Group in the International Energy Agency's (IEA's) Hydrogen Implementing Agreement on photoelectrolytic hydrogen production.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Material Durability
- N. Materials and System Engineering
- O. Photoelectrochemical Efficiency

Approach

- Using new and existing high-throughput synthesis and screening technology, create and screen suitable new mixed metal oxide materials for electrochemical/photoelectrochemical hydrogen production.
- Improve and expand the chemical synthesis routes developed for automated high-throughput experimentation.
- Utilize the automated synthesis systems to create libraries of potential hydrogen electrocatalysts/ photocatalysts.

- Rapidly screen libraries for potential materials with electrocatalytic and/or photoelectrocatalytic activity.
- Synthesize, using conventional routes, selected materials identified in libraries for detailed structural and electronic analysis.

Accomplishments

- Designed and fabricated combinatorial chemistry systems for synthesis and screening of hydrogen production photocatalysts (Figures 1a, 1b).
- Demonstrated that compositional and preparative modifications of known metal oxide hosts may improve their photoelectrocatalytic properties (Figure 2).
- Achieved first electrochemical synthesis of ordered nanoporous metal oxides (Figure 5).
- Discovered nanoparticulate Pt/WO_3, which is photoactive and resistant to CO poisoning.
- Developed methods for and demonstrated controlled electrosynthesis of high-activity Au nanocluster catalysts.
- Identified H intercalation as a critical component of poisoning resistance of metal oxide electrocatalysts.

Future Directions

- Expand the exploration of new materials with the parallel synthesis and screening systems with particular emphasis on expanding the exploration of the composition-function relationships of quartenary ZnO systems.
- Develop an automated spray pyrolysis methodology and system as a means of high-throughput synthesis and demonstrate the system for dopants in iron-based hosts.
- Expand the search for improved photoelectrochemical performance from nanoporous/nanoparticulate morphologies of known hosts.
- Using calibrated standards, obtain quantitative values of the efficiencies of the materials under investigation in terms of electrons per photon and power efficiency.
- Begin definition and design of photoelectrochemical reactor systems which can incorporate the new materials, and perform preliminary process design calculations on a large-scale hydrogen plant to establish cost estimate models.

Introduction

The overall project objective is to utilize combinatorial material science to expedite the discovery of an efficient, practical, and economically sensible material for the photoelectrochemical production of hydrogen from water and sunlight. This represents a shift in the research paradigm from conventional serial chemical research to a combinatorial approach that features systematic and high-speed exploration of new metal-oxide based solid-state materials. By investigating large arrays of diverse materials, we are working to improve the understanding of the fundamental mechanisms and composition-structure-property relationships within these systems while discovering new and useful energy-producing photocatalysts.

Approach

As we have developed automated chemical synthesis and screening systems during the first two years of the program, in the second year we have focused on the preparation and analysis of diverse metal-oxide libraries with semiconducting and other properties suitable for photoelectrocatalysis. Diversity has included (1) variations in composition (by variable doping, electrochemical synthesis

conditions, and surface redox catalysts) and (2) variations in structure (by deliberate and diverse ionic and non-ionic templating agents, synthesis conditions, and doping). The libraries are primarily screened by photoelectrochemical methods, including zero-bias photocurrent and cyclic photovoltammetry.

Results

Task 1. We created tungsten-molybdenum mixed oxide libraries ($W_{1-x}Mo_xO_3$) using a parallel synthesis method. The film compositions were readily controlled by varying the ratios of the two metals in the electrolyte. By X-ray diffraction patterns and Raman spectroscopy, atomically-mixed metal oxides were confirmed to exist rather than simply mixed phases of pure tungsten oxide and pure molybdenum oxide (Figure 2). Zero-bias photocurrents of the mixed oxides were strongly dependent on the film composition. The maximum photoresponse was observed with $W_{0.5}Mo_{0.5}O_3$, and photoactivity decreased as film composition approached either pure oxide. The photoresponse of the $W_{0.5}Mo_{0.5}O_3$ mixed oxide film, 18.5 μA/cm^2, was 50.4% higher than that of the pure tungsten oxide film. Cation intercalations were carried out for

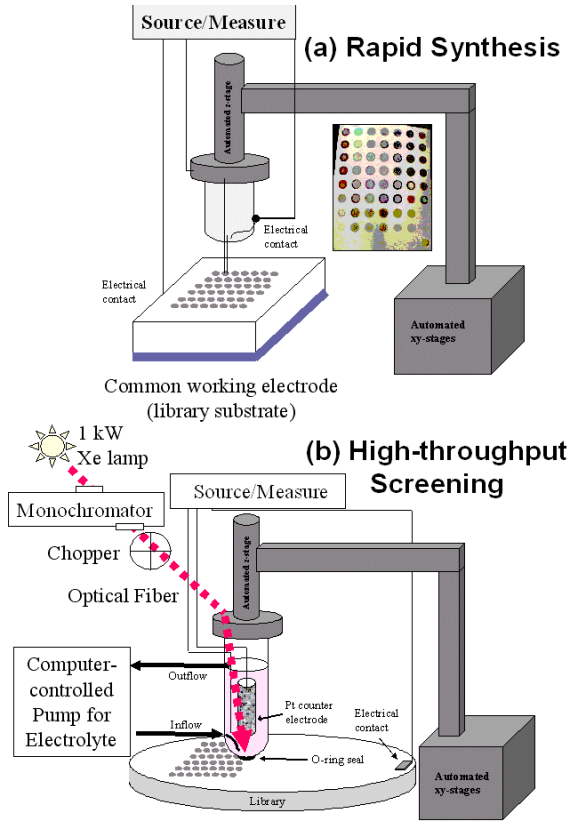

Figure 1. Automated Electrochemical Synthesis and Screening: (a) Rapid synthesis - a perforated polypropylene block with 63 independent o-rings is sealed upon a substrate, allowing for 63 distinct electrolyte compositions. A probe with reference and counter electrodes are automatically dipped into each bath, and a potentiostat conducts electrodeposition of each sample. (b) High-throughput screening - a scanning photoelectrochemical cell traverses a library, illuminating each sample with a chopped light source, and photocurrent is measured.

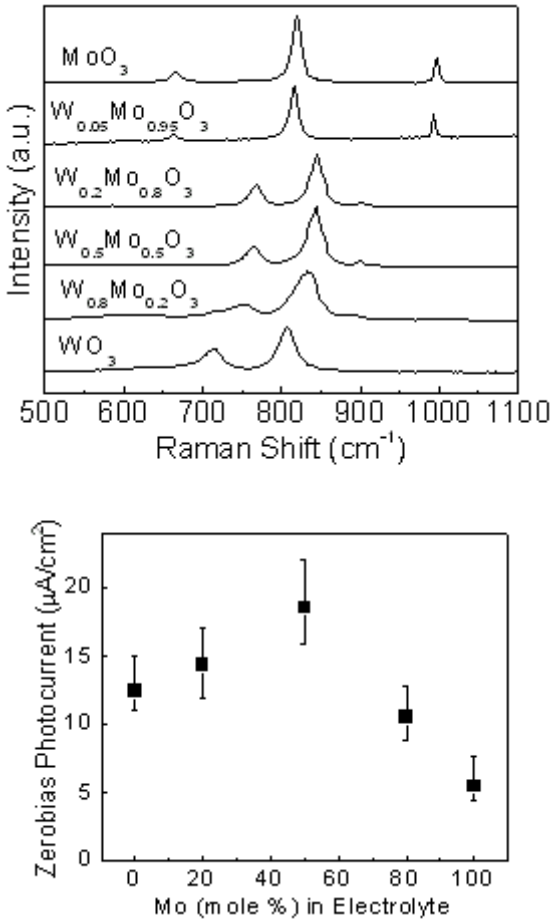

Figure 2. (top) Raman spectroscopy of tungsten-molybdenum mixed oxides with respect to film compositions and (bottom) Zero-bias photocurrent of tungsten-molybdenum mixed metal oxide films. All samples were n-type semiconductors. Illumination was provided by a 150-W Xe lamp.

the tungsten-molybdenum mixed oxide library using H^+, Li^+, Na^+, and K^+. Interestingly, as the ratio of tungsten to molybdenum approaches unity, electrochromic properties improve. Compared to either pure tungsten oxide or pure molybdenum oxide, the mixed oxides show considerably enhanced intercalation properties, with the $W_{0.5}Mo_{0.5}O_3$ film exhibiting the highest intercalation properties of all. Metal oxide libraries were also successfully synthesized by electroless deposition on copper substrates from metal peroxo electrolytes (WO_3, MoO_3, ZrO_2, Nb_2O_5). The reducing electrons were provided by the copper substrate as it was oxidized to CuO.

Task 2. Several hundred samples of different ZnO-based materials have been synthesized and screened for zero-bias photocurrent. All materials were binary systems consisting of ZnO and a single other element – typically a transition metal – and a range of dopant concentrations was explored for each element. The aim of the dopant is to improve upon the photocatalytic activity of ZnO, particularly under visible illumination, and to increase the stability of the material. Table 1 has been constructed to qualitatively indicate the impact of the dopants on the material properties vs. pure ZnO ("very poor", "poor", "average", "good", and "excellent"). Cobalt showed the greatest improvements in terms of visible light photocurrent, and the photoactivity of cerium samples remained high for several minutes, as opposed to pure ZnO, whose photocurrent decayed to 15% of its initial value after the same amount of time. Iron, nickel, ruthenium, and manganese also showed improvements to ZnO. After having explored 24 different binary ZnO systems, of different concentrations, we are looking forward to focusing on the best materials to begin our investigation of ternary and quaternary libraries.

Task 3. Diverse compositions of cobalt-iron-nickel oxide materials supported on 304 stainless steel have been synthesized by combinatorial spray pyrolysis. These samples have been studied for water oxidation electrocatalysis by tafel slopes and exchange current in basic electrolytes (KOH 20% w/w). Different precursor solutions were used to create compositional differences. The best electrocatalysts found to date in this study were synthesized with iron or nickel at 10-20% of the cobalt concentration in solution. Ternary libraries will be explored in the near future.

Tasks 4 & 5. We are currently completing our infrastructure for the automated measurement of bandgap of combinatorial libraries. The system is shown schematically in Figure 3. In this design, an integrating sphere is affixed to our x-y-z combinatorial stages. In a fully automated fashion, the integrating sphere steps down upon each sample independently, and each sample is illuminated by a 1-kW Xe lamp (ThermoOriel). An optical fiber carries the diffuse reflectance of the sample to an Ocean Optics S2000 detector, which measures the spectra and allows for bandgap calculation. This combinatorial method for bandgap measurement will be the first screening conducted on libraries.

Task 6. Heterostructures of Cu_2O/TiO_2 have been synthesized and screened for photocatalytic activity.

Table 1. Qualitative impact (excellent, good, average, poor, very poor) of 24 different elements when co-deposited with ZnO as compared to pure ZnO.

Co-deposited species with ZnO	Visible Photocurrent	UV-Vis Photocurrent	Stability
Ag	Poor	Poor	Average
Al	Good	Average	Good
Au	Poor	Poor	Average
Ce	Average	Average	Excellent
Cd	Poor	Poor	Average
Co	Excellent	Poor	Good
Cr	Poor	Poor	Average
Cu	Poor	Poor	Average
Eu	Poor	Poor	Average
Fe	Good	Good	Average
Mn	Average	Average	Good
Mo	Poor	Poor	Poor
Ni	Excellent	Excellent	Average
Nb	Poor	Average	Good
Pd	Very Poor	Very Poor	N/A
Pt	Poor	Poor	Poor
Rh	Poor	Poor	Aveage
Ru	Excellent	Excellent	Average
Sb	Poor	Poor	Average
Sn	Average	Average	Good
Ti	Very Poor	Very Poor	N/A
V	Poor	Poor	Average
W	N/A	N/A	N/A
Zr	Average	Average	Good

The Cu_2O/TiO_2 heterojunction scheme can be viewed in Figure 4. Cu_2O is a photocatalyst that benefits from a small bandgap (2.0 eV), which allows for excellent solar absorption. It is limited, however, by photocorrosion which degrades the material rapidly. TiO_2, on the other hand, is a robust photocatalyst that is stable for long periods of time (ca. thousands of hours); however, it is limited by poor visible photon absorption (bandgap 3.0 eV). By creating a heterojuction of Cu_2O covered with TiO_2, a photocatalytic system (which operates as a photocathode) results which absorbs more visible light than pure Cu_2O and is as stable as pure TiO_2.

Task 7. We have been developing a general method for the production of high surface area nanostructured films by utilizing electrochemically-driven self-assembly of surfactants. We have successfully electrodeposited mesoporous WO_3, TiO_2 by controlling deposition conditions (Figure 5). Mesoporous tungsten oxide films with lamellar structure were successfully synthesized by electrodeposition using sodium dodecylsulphate (SDS) as a templating agent. Nanophases can be varied by changing the deposition potential, which directly affects the surface charge densities of the electrode and, therefore, the surface assembly patterns of the inorganic-surfactant aggregates. Compared to nonporous tungsten oxide prepared with isopropanol, lamellar phase mesoporous tungsten oxide showed higher photocatalytic activity and greater current density for hydrogen intercalation. Functional improvements are most probably due to the larger surface area of mesoporous tungsten oxide and facilitated charge transport.

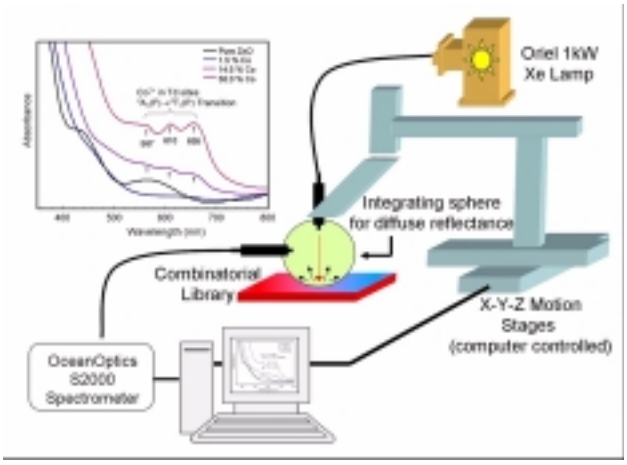

Figure 3. Schematic design of combinatorial measurement of diffuse reflectance for ultraviolet-vis spectroscopy and bandgap calculation.

Task 8. We have actively contributed to the Annex 14 of the IEA, including attendance and participation in the expert meeting in Paris, France, April 27-28. Results were presented to the Annex working group from our laboratory, and we shared ideas concerning the future of international collaboration in the area of photoelectrochemical water splitting.

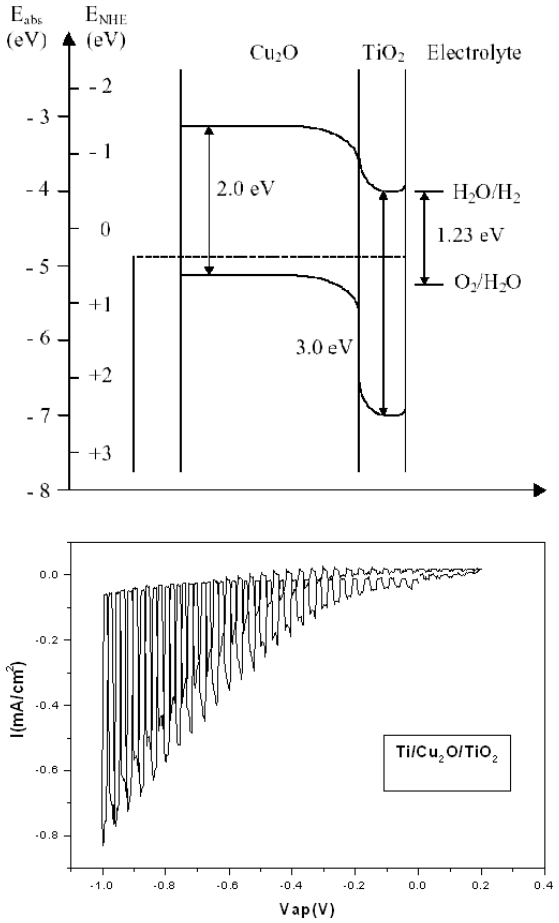

Figure 4. Cu_2O/TiO_2 Heterojunction on Ti Foil: (top) The Cu_2O functions as a light absorber and the TiO_2 overlayer protects against corrosion. The band diagram demonstrates why the device operates as a photocathode despite n-type TiO_2 on the surface. (bottom) The device produces nearly 1 mA/cm^2 of photocurrent at –1 V bias vs. Ag/AgCl under 1 sun illumination.

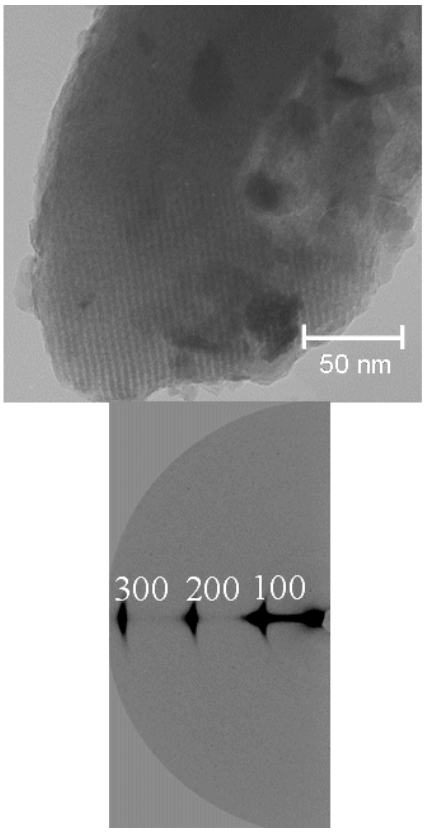

Figure 5. Nanoporous Metal Oxide Photocatalyts: (top) Transition electron microscopy images of tungsten oxide films deposited in the presence of SDS and (bottom) 2D-grazing incidence x-ray diffraction pattern of lamellar tungsten oxide on indium tin oxide coated glass.

Conclusions

As we complete the second year of the project in the fall of 2003, we will have developed combinatorial methods for high-throughput synthesis and screening of new mixed-metal oxides active for photoelectrochemical production of hydrogen. Mixed WO_3-MoO_3 has shown improvements over the pure oxide components, and binary ZnO:Me (Me = Co, Ni, Fe, Ru, Ce, Mn) have demonstrated improved photocatalytic performance compared to pure ZnO. A new means of nanoporous metal oxide synthesis has been demonstrated and Pt and Au nanoparticles created electrochemically which show promise as new surface electrocatalysts.

FY 2003 Publications/Presentations

1. S.-H. Baeck, T. Jaramillo, G. Stucky, and E. McFarland, "Controlled Synthesis of Nanoparticulate Tungsten Oxide", Nano Letters, 2(8), 831-834(2002).

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3. S.-H. Baeck, T. Jaramillo, and E. McFarland, "Influence of Composition and Morphology on Photo and Electrocatalytic Activity of Electrodeposited Pt/WO_3", Abstracts of Papers of American Chemical Society, 224: 062-FUEL Part 1 (2002).

4. S.-H. Baeck and E. McFarland, "Combinatorial Electrochemical Synthesis and Characterization of Tungsten-Molybdenum Mixed Oxides," Korean Journal of Chemical Engineering, 19 (4), 593-596 (2002).

5. K.-S. Choi, H. Lichtenegger, G. Stucky, and E. McFarland, "Electrochemical Synthesis of Nanostructured ZnO Films Utilizing Self-Assembly of Surfactant Molecules at Solid-Liquid Interfaces", Journal of the American Chemical Society, 124(42), 12402-12403 (2002).

6. W. Siripala, A. Ivanovskaya, T. Jaramillo, S.-H. Baeck, and E. McFarland," A Cu_2O/TiO_2 Hetrojuction Thin Film Cathode for Photoelectrocatalysis", Solar Energy Materials & Solar Cells, 77(3), 229-237 (2003).

7. T. Jaramillo, S.-H. Baeck, B.R. Cuenya, and E. McFarland, "Catalytic Activity of Supported Au Nanoparticles Deposited From Block Co-polymer Micelles", Journal of the American Chemical Society, 125(24), 7148-7149 (2003).

8. K.-S. Choi, E. McFarland, and G. Stucky, "Electrocatalytic Properties of Thin Mesoporous Platinum Films Synthesized Utilizing Potential-

Controlled Surfactant Assembly", Advanced Materials, Accepted and in Press (2003).

9. S.-H. Baeck, K.-S. Choi, T. Jaramillo, G. Stucky, and E. McFarland, "Enhancement of Photocatalytic and Electrochromic Properties of Electrochemically Fabricated Mesoporous WO_3 Thin Films", Advanced Materials, Accepted and in Press (2003 August).

10. S.-H. Baeck, T. Jaramillo, G. Stucky, and E. McFarland, "Synthesis of Tungsten Oxide on Copper Surfaces by Electroless Deposition", Chemistry of Materials, Accepted and in Press (2003 August).